Supplementary Information

X-Shaped Thiadiazole-Containing Double [7]Heterohelicene with Strong Chiroptical Response and π-Stacked Homochiral Assembly

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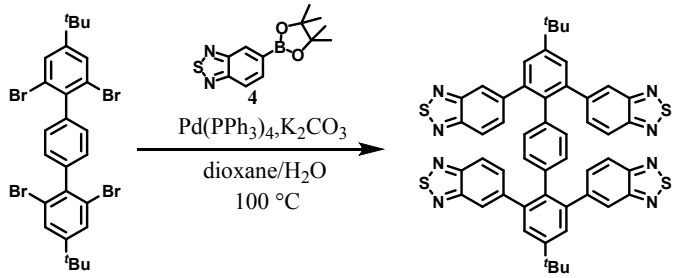
Tabel of Contents

1. Experimental Section

General Methods

Unless otherwise noted，all reagents and solvents were purchased from Energy Chemicals, Chron Chemicals or Sigma-Aldrich, and used without further purification. 2,2”,6,6”-Tetrabromo-4,4”-di-*tert*-butyl-1,1’:4’,1”- terphenyl (**3**) was prepared according to the literature procedures.[1] NMR spectra were recorded on Bruker Avance 400 (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz). The signals have been designated as follows: s (singlet), d (doublet), t (triplet). High resolution mass spectrometry (HRMS) was performed on a SolariX Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer by matrix-assisted laser desorption/ionization (MALDI). UV-Vis absorption spectra were recorded by UV-2600 Spectrophotometer. Fluorescence spectra were measured by HITACHI F-4600 Fluorescence Spectrophotometer. Absolute photoluminescence quantum yields were determined on Edinburgh FS5 Fluorescence Spectrometer. Fluorescence lifetimes were determined by transient state fluorescence spectroscopy on Edinburgh FLS1000 fluorescence spectrometer. Optical resolution of the enantiomers of **1** was performed on a Shimadzu LC-16A instrument equipped with a DAICEL CHIRALPAK IE column. A mixture of chloroform/hexane was used as the eluent. Circular dichroism (CD) spectra were collected on JASCO J-810 circular dichroism spectrometer at 298 K. X-ray crystallography was performed on a Bruker AXS Kappa ApexII Duo Diffractometer.

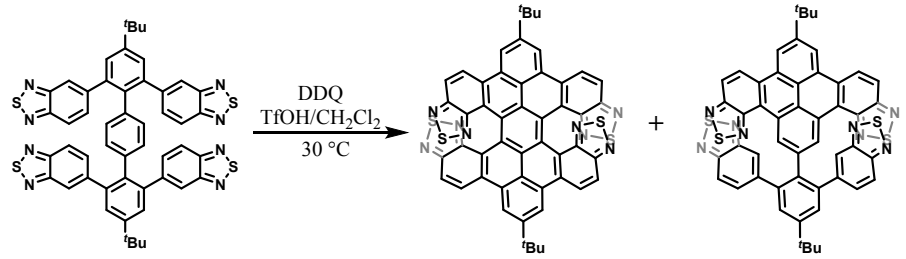
Synthesis



3 **TBTP**

5,5',5'',5'''-(4,4''-Di-*tert*-butyl-[1,1':4',1''-terphenyl]-2,2'',6,6''-tetrayl)tetrakis(benzo[*c*][1,2,5]thiadiazole) (TBTP)： Under argon atmosphere, 2,2”,6,6”-tetrabromo-4,4”-di-*tert*-butyl-1,1’:4’,1”-terphenyl (**3**, 500 mg, 0.760 mmol), benzothiadiazole boronic ester (**4**, 1.59 g, 6.08 mmol), potassium carbonate (1.62 g, 11.7 mmol), and $Pd(pph_3)_4$ (110 mg, 0.0952 mmol) were dissolved in a degassed solvent mixture of dioxane (48 mL) and H_2O (7 mL). The resulting solution was stirred at 100 °C for 24 h. After cooled to room temperature, the reaction mixture was poured into water and extracted with dichloromethane. The combined organic phases were washed with water and brine, and evaporated under vacuum. The residue was purified by chromatography on silica gel using petroleum ether / dichloromethane (1/4) as eluent to obtain the title compound as white solid. (534 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm) δ 7.87 (d, J = 9.1 Hz, 4H), 7.82 (s, 4H), 7.50 (s, 4H), 7.06 (d, J = 9.1 Hz, 4H), 6.52 (s, 4H), 1.39 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, ppm) δ 154.88, 153.71, 151.22, 144.10, 140.08, 136.39, 135.11, 132.74, 131.57, 128.17, 121.57, 120.12, 34.81, 31.30; HRMS (MALDI-TOF) *m/z*: Calcd

for $C_{50}H_{39}N_8S_4$: 879.2181; Found: 879.2173 ($[M+H]^+$).



TBTP **1** **2**

Double thiadiazolo[7]helicene 1 and partially fused compound 2: Under argon atmosphere, **TBTP** (200 mg, 0.227 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (515 mg, 2.27 mmol) were dissolved in 150 mL of degassed anhydrous dichloromethane. The resulting solution was cooled to 0 °C and triflic acid (5.2 mL) was added dropwise. The reaction mixture was then heated to 30 °C and stirred overnight. After cooled to room temperature, the reaction mixture was neutralized by triethylamine, and diluted with dichloromethane The organic phases were combined, washed with water, and evaporated to dryness. The residue was purified by silica gel chromatography using petroleum ether / dichloromethane (1/2) as the eluent to obtain compound **1** (100 mg, 50% yield) and **2** (50 mg, 25% yield) as red and yellow solids, respectively. Compound **1**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm) δ 9.46 (s, 4H), 9.30 (d, J = 9.5 Hz, 4H), 8.13 (d, J = 9.4 Hz, 4H), 1.88 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, ppm) δ 153.84, 152.80, 150.16, 129.98, 128.74, 127.54, 125.87, 124.30, 122.31, 121.95, 121.80, 119.91, 36.09, 32.11; HRMS (MALDI-TOF) *m/z*: Calcd for $C_{50}H_{30}N_8S_4$: 870.1455; Found: 870.1490 (M^+). Compound **2**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm) δ 10.73 (s, 2H), 9.13 (s, 2H), 9.04 (d, J = 9.6 Hz, 2H), 8.41 (s, 2H), 8.16 (d, J = 9.5 Hz, 2H), 7.88 (s, 2H), 7.17 (d, J = 9.1 Hz, 2H), 7.13 (d, J = 10.4 Hz, 2H), 1.71 (s, 9H), 1.60 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.18, 154.11, 152.53, 152.45, 150.56, 148.54, 143.65, 140.23, 136.55, 136.01, 132.08, 130.98, 129.54, 127.53, 127.41, 126.17, 125.88, 122.74, 122.10, 121.66, 121.43, 119.83, 119.58, 118.35, 34.86, 34.04, 30.93, 30.51; HRMS (MALDI-TOF) *m/z*: Calcd for $C_{50}H_{34}N_8S_4$: 874.1789; Found: 874.1779 (M^+).

2. Optical Resolution

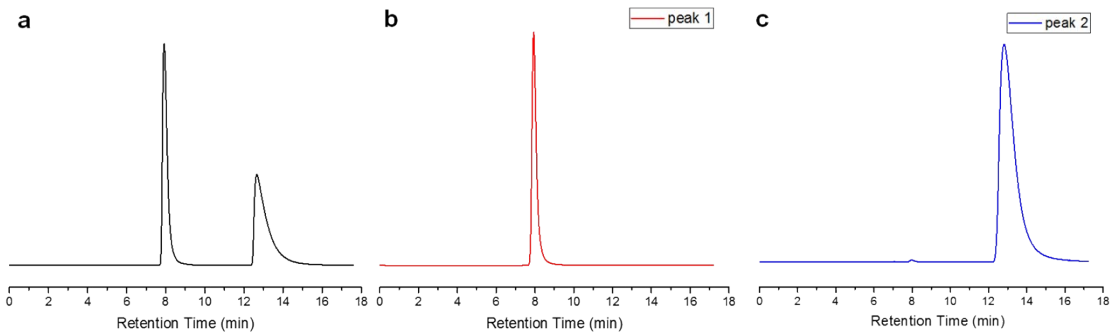


Figure S1. Chiral HPLC traces for the separation of racemic **1** (a), the first eluting enantiomer (b) and the second eluting enantiomer (c) using chloroform as eluent with a flow rate of 0.5 mL/min.

3. X-ray single crystallography

The single crystals of racemic **1**, (*M*,*M*)**-1** and **2** suitable for X-ray analysis were obtained as follows. Single crystal of racemic **1** was grown by diffusing methanol vapor into the chloroform solution. Single crystal of (*M*,*M*)**-1** was grown by slowly evaporating the dichloromethane/methanol solution. Single crystal of compound **2** was grown by diffusing methanol vapor into the toluene solution. All these crystal structures were deposited at the Cambridge Crystallographic Data Centre and the data can be obtained free of charge via www.ccdc.cam.ac.uk/structures.

Table S1. Crystal data for racemic **1** (CCDC number: 2024521).

formula	$C_{50}H_{30}N_8S_4$, 2($CHCl_3$)
molecular weight	871.09 g mol^{-1}
absorption	μ=0.573mm^{-1}
crystal size	red block with undefined size
space group	P-1(triclinic)
lattice parameters (calculate from 7777 reflections with 2.35°< θ <24.99°)	a=12.6199(3)Å α= 89.8620(10)° b=12.6719(3)Å β=78.768(10)° c=16.2469(3)Å γ=73.0990(10)° v=2434.27(9)$Å^3$ z=2 F(000)=1132.0
temperature	296(2) k
density	d_{xray}=1.514g cm^{-3}
<u>data collection</u>	
diffractometer	Bruker APEX-II CCD
radiation	Mo-K_α Graphitmonochromator
scan-type	ω scans
scan-width	1°
scan range	1.28°≤θ<27.7° -16°≤ h ≤ 16°-16° ≤ k ≤ 16° -21°≤ l ≤ 21°

number of reflections:	
measured	41534
unique	11170(R_{int}=0.0456)
observed	5608(I/s(I)>2)
Data correction, structure solution and refinement	
corrections	Bruker APEX2
structure solution	program:SHELXS-97 (sheldrick, 1990)
refinement	program: SHELXS-97 (sheldrick, 1997). 631 refined parameters, weighting scheme: $w=1/[\sigma^2(F_o^2)+(0.1484P)^2+2.3560P]$ where $P=(F_o^2+2F_c^2)/3$
R-values	wR_2=0.2369 (R=0.0879 for observed reflections, 0.1720 for all reflections)
goodness of fit	S=1.033

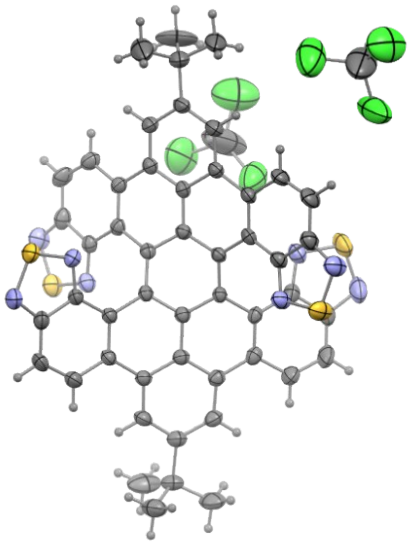


Figure S2. ORTEP drawing of **1** in racemic crystal with 50% probability thermal ellipsoids.

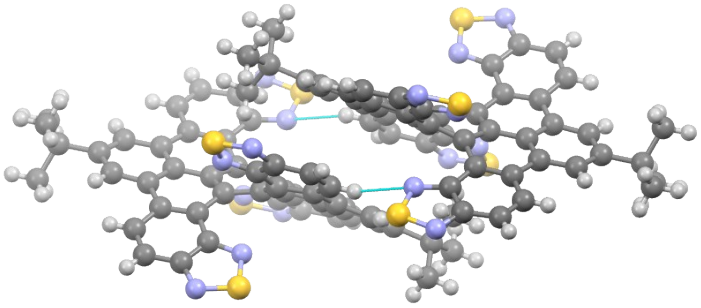


Figure S3. Heterochiral dimer stacked by π-π interactions and C-H···N contacts (blue dotted lines) of **1** in racemic crystal.

TableS2. Crystal data for (*M*,*M*)-**1** (CCDC number: 2024494).

formula	$C_{50}H_{30}N_8S_4$, C_7H_8
molecular weight	871.09 g mol^{-1}
absorption	μ=0.234 mm^{-1}
crystal size	0.29×0.11×0.07 mm^3(yellow needle)
space group	P2yb(monoclinic)
lattice parameters (calculate from 108 reflections with 2.41°< θ <11.0°)	a=24.74(8)Å α= 90 (10)° b=8.05(2)Å β=94.46(6)° c=25.10(9)Å γ=90 (10)° v=4983(28)$Å^3$ z=2 F(000)=1898.0
temperature	150(2) k
density	d_{xray}=1.222 g cm^{-3}
data collection	
diffractometer	Bruker APEX-II CCD
radiation	Mo-K_αGraphitmonochromator
scan-type	ω scans
scan-width	1°
scan range	2.23°≤θ<25° -29°≤ h ≤ 29°-9° ≤ k ≤ 9° -29°≤ l ≤ 29°
number of reflections:	
measured	149715
unique	17558(R_{int}=0.1440)
observed	13842(I/s(I)>2)
Data correction, structure solution and refinement	
corrections	Bruker APEX2
structure solution	program: SHELXS-97 (Sheldrick, 2008)

refinement	program: SAINT V8.38A (Sheldrick, 2016). 1193 refined parameters, weighting scheme: $w=1/[\sigma^2(F_o^2)+(0.1309P)^2]$ where $P=(F_o^2+2F_c^2)/3$
R-values	wR_2=0.1857 (R=0.0694 for observed reflections, 0.0889 for all reflections)
goodness of fit	S=1.062

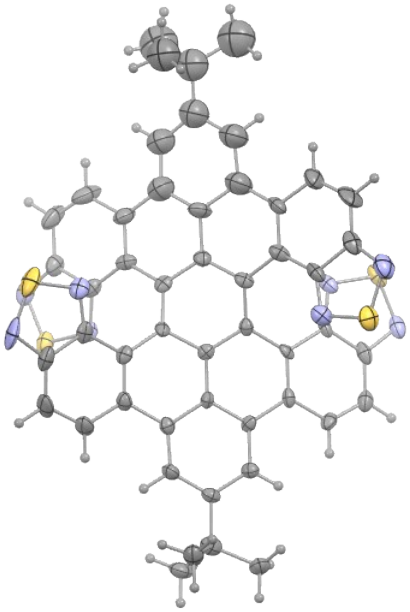


Figure S4. ORTEP drawing of (*M*,*M*)-**1** in enantiopure crystal with 50% probability thermal ellipsoids.

Table S3. Crystal data for compound **2** (CCDC number: 2024495).

formula	$C_{50}H_{34}N_8S_4$, CH_2Cl_2
molecular weight	875.09 g mol^{-1}
absorption	μ=0.308mm^{-1}
crystal size	0.22×0.06×0.03mm^3(yellow block)
space group	P-1(Triclinic)
lattice parameters (calculate from 2154 reflections with 2.74°< θ <18.51°)	a= 15.056(3)Å α= 94.827(14)° b= 16.373(3) Å β =107.933(12)° c= 19.923(4)Å γ=94.992(13)° v=4622.9(16)$Å^3$ z=2 F(000)=1900.0
temperature	296(2) k
density	d_{xray}=1.318gcm^{-3}
<u>data collection</u>	

diffractometer	Bruker APEX-II CCD
radiation	Mo-K_α Graphitmonochromator
scan-type	ω scans
scan-width	1 °
scan range	1.4°≤θ<25° -17°≤ h ≤ 17°-19° ≤ k ≤ 19° -23°≤ l ≤ 23°
number of reflections:	
measured	63549
unique	17562(R_{int}=0.1718)
observed	2154(I/s(I)>2)
Data correction, structure solution and refinement	
corrections	Bruker APEX2
structure solution	program: SHELXS-97 (Sheldrick, 2008)
refinement	program: SHELXL-2014/7 (Sheldrick, 2014). 1171 refined parameters, weighting scheme: $w=1/[\sigma^2(F_o^2)+(0.1309P)^2]$ where $P=(F_o^2+2F_c^2)/3$
R-values	wR_2=0.1680 (R=0.0840 for observed reflections, 0.2487 for all reflections)
goodness of fit	S=0.852

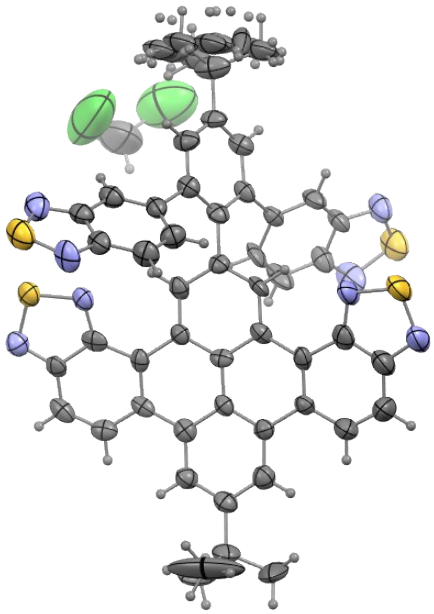


Figure S5. ORTEP drawing of **2** with 50% probability (the *tert*-butyl groups are disordered).

4. DFT calculations and Optical Properties

DFT calculations were performed using the Gaussian 09 software package.[2] Spin density calculation of the radical cation of precursor **3** was performed at the UB3LYP/6-31g(d,p) level of theory. The geometries, molecular orbitals (MO), and MO energies of **1** were calculated at the B3LYP/6-311G(d,p) level. The UV-vis absorption and CD spectra were simulated by time-dependent DFT (TD-DFT) calculations at the same level of theory.

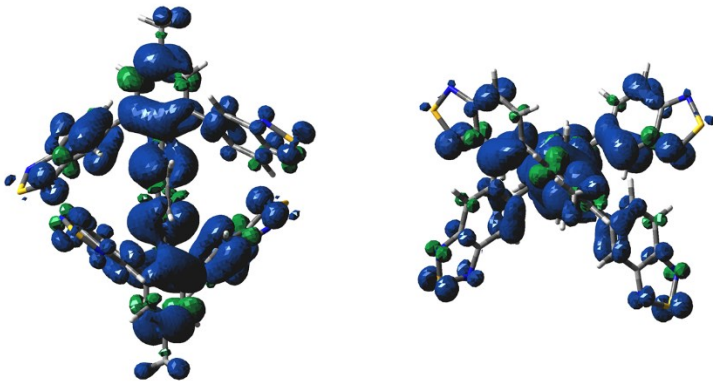


Figure S6. Spin-density distribution (top and side views) of the radical cation of precursor **3**

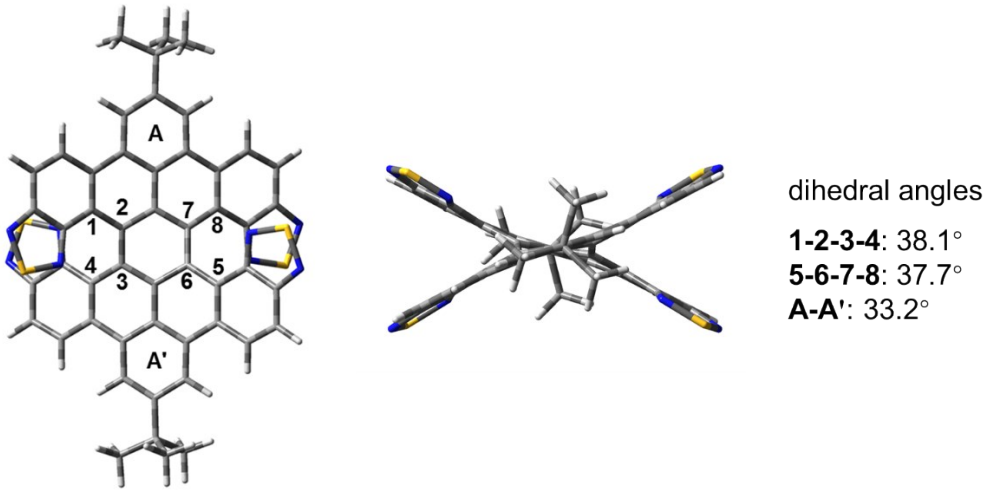


Figure S7. Top and side views of the optimized geometry of **1** (relative dihedral angles are listed).

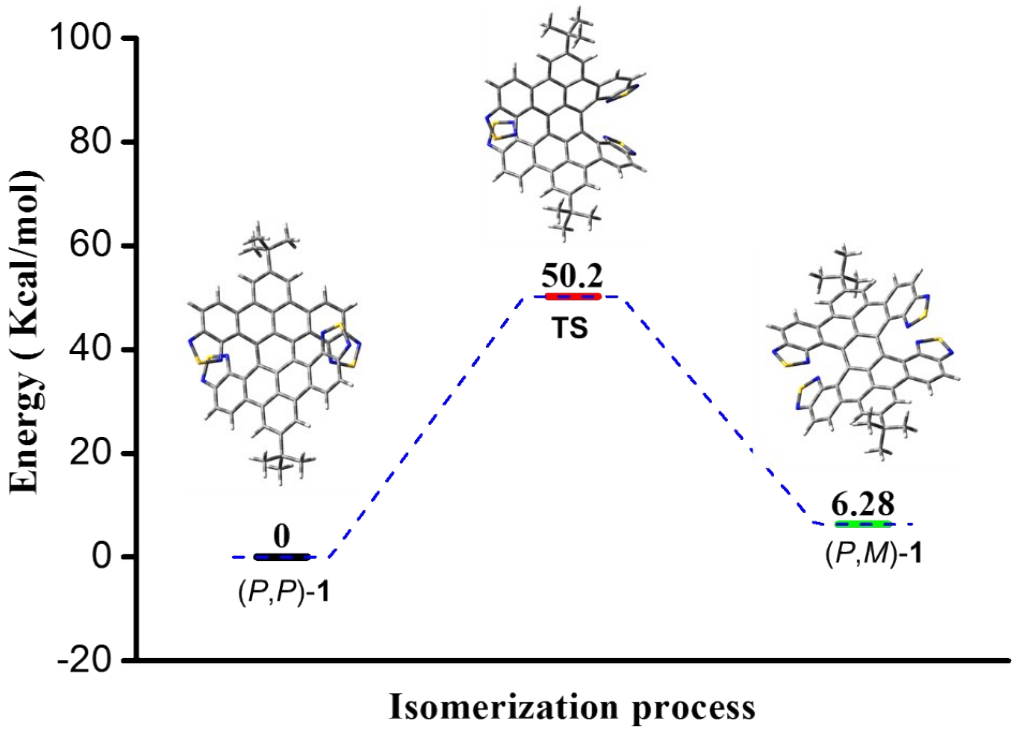


Figure S8. Relative Energy diagrams of the isomerization process from (*P*,*P*)-**1** to (*M*,*M*)-**1** through a transition state (TS).

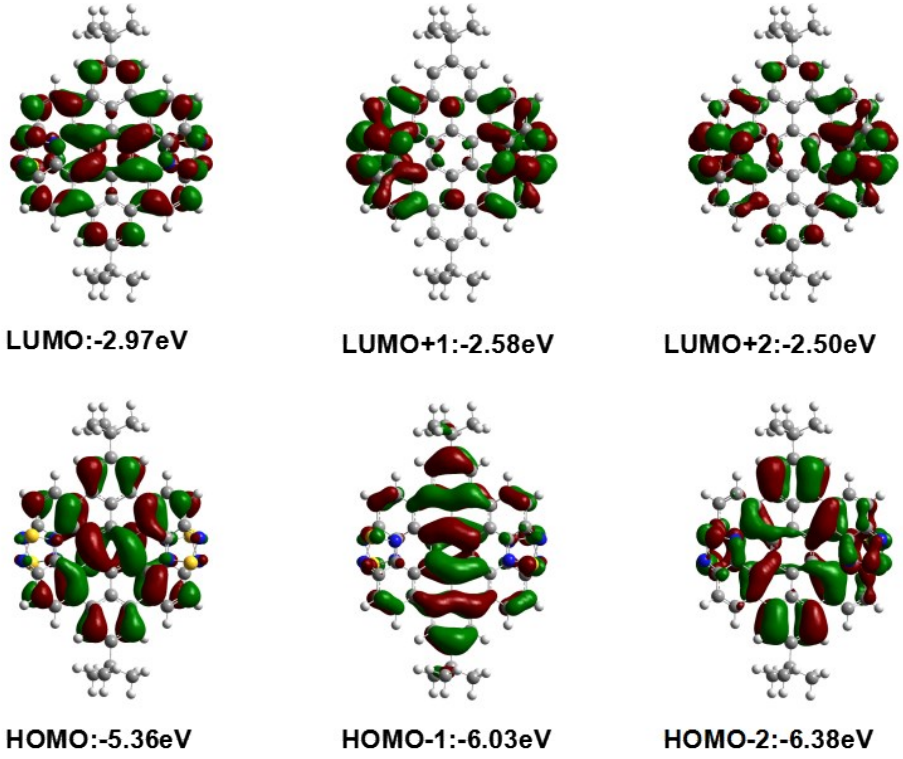


Figure S9. Calculated molecular orbitals and energy diagrams of **1**.

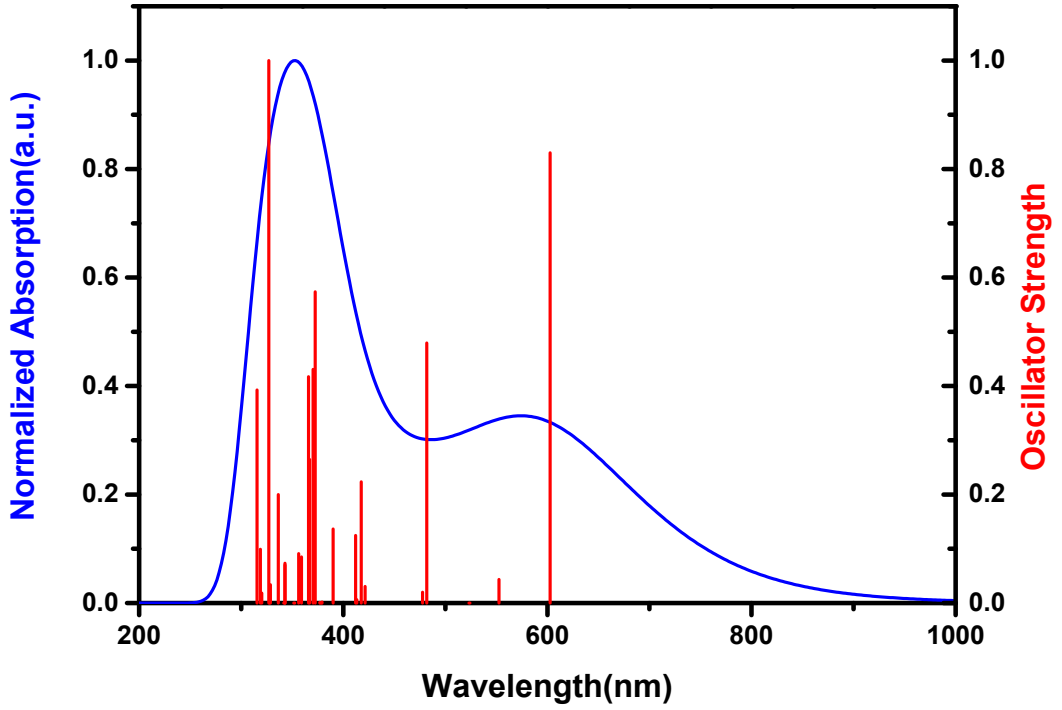


Figure S10. Simulated UV-vis spectrum and vertical transitions of **1** by TD-DFT calculation.

Table S4. Major excited states of **1** calculated by TD-DFT.

excited state	energy (eV)	wavelength (nm)	oscillator strength (*f*)	description
1	2.0571	602.71	0.2080	H→L(0.69977)
2	2.5733	481.81	0.1202	H-1→L(0.66306) H→L+4(-0.21383)
3	2.9688	417.62	0.0561	H-3→L(0.66328) H-2→L(-0.21396)
4	3.3290	372.43	0.1438	H-1→L(0.15616) H-1→L+3(0.43624) H→L+4(0.49253)
5	3.3475	370.38	0.1080	H-1→L(-0.12245) H-1→L+3(0.53506) H→L+4(-0.39399)
6	3.3782	367.02	0.0664	H-6→L(0.52732) H-5→L(-0.12580) H-3→L+1(-0.25852) H-3→L+2(0.13808) H-2→L+2(-0.16710) H→L+5(0.24181)
7	3.3877	365.99	0.1046	H-6→L(0.40643) H-5→L(0.20698) H-3→L+1(0.36365) H-3L+2(0.11643) H-2L+2(0.12537) H-1L+4(0.13183) HL+5(-0.29517)
8	3.6867	336.30	0.0502	H-6→L+2(0.11519) H-5→L+1(0.46720) H-4→L+2(-0.25545) H-2→L+3(-0.42648)

9	3.7913	327.02	0.2506	H-5→L+1(0.46232) H-4→L+2(0.35911) H-3→L+3(0.15064) H-2→L+3(0.26977) H→L+4(-0.12706)
10	3.9304	315.45	0.0985	H-8→L(-0.11482) H-6→L+1(-0.11033) H-6→L+2(0.64464) H-5→L+2(0.13840) H-2→L+3(0.10761)

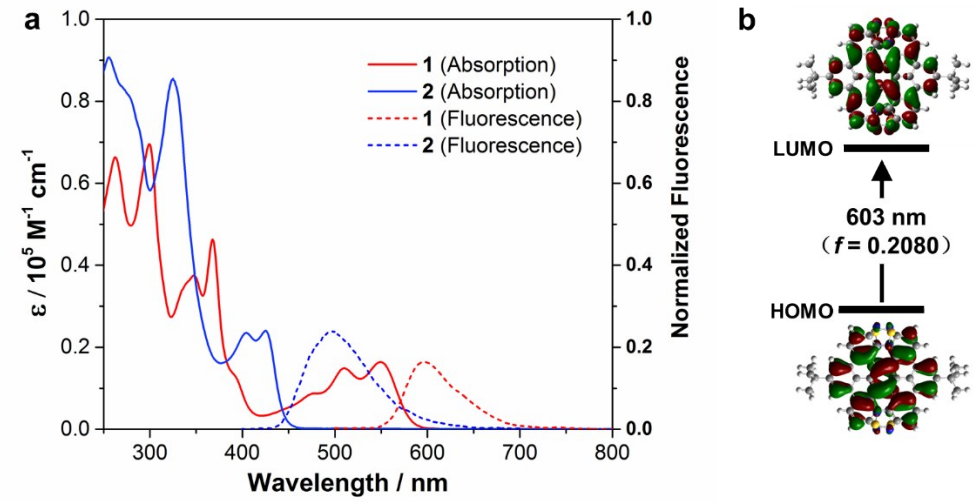


Figure S11. (a) UV-Vis absorption (solid lines) and emission (dotted lines) spectra of compounds **1** and **2** in chloroform with the concentration of 1×10^{-5} M. (b) the molecular orbitals and electronic transition diagram of **1**.

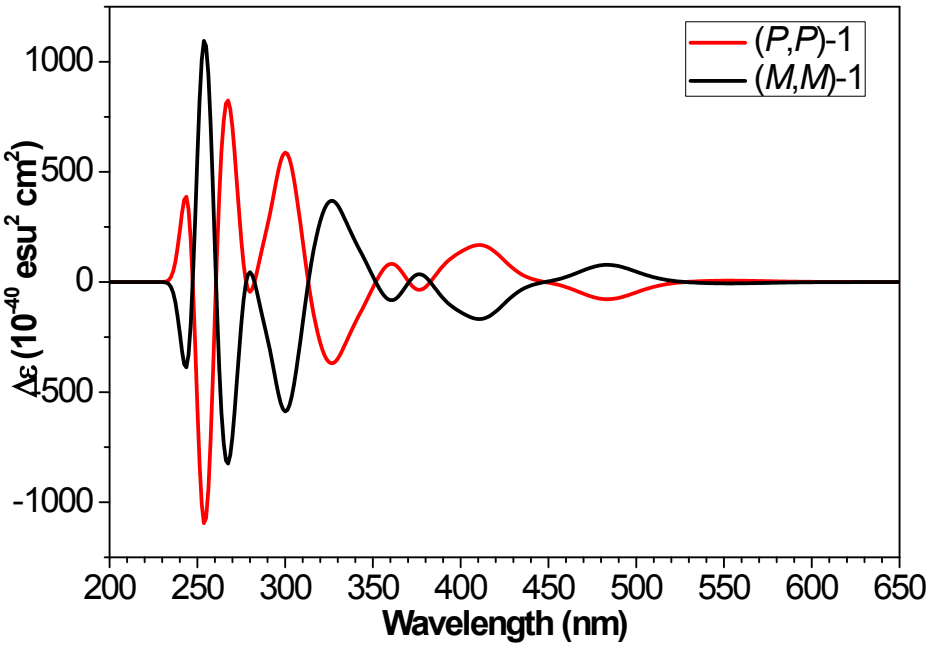


Figure S12. Simulated CD spectra of (*P*,*P*)-**1** and (*M*,*M*)-**1** by TD-DFT calculation.

Table S5 . Chiroptical properties calculations of (*M*,*M*)-**1** calculated by TD-DFT.

excited state	μ (10^{-20} esu·cm)	m (10^{-20} erg/Gauss)	cos ($\theta_{\mu,m}$)	$g_{abs,cal}$	wavelength (nm)
1	516.95	0.022	-0.024	-0.00000414	602.71
2	113.67	0.099	-1.000	-0.003	481.81
3	8.62	0.011	1.000	0.005	417.62
4	351.21	0.501	1.000	0.006	372.43
5	72.12	0.341	-0.993	-0.019	370.38
6	83.74	0.151	-0.763	-0.006	367.02
7	223.47	0.125	-1.000	-0.002	365.99
8	37.57	0.054	-1.000	-0.006	336.30
9	165.80	1.366	-0.999	-0.033	327.02
10	168.89	0.918	-1.000	-0.022	315.45

μ: transition electric dipole moments.
m: transition magnetic dipole moments.
$\theta_{\mu,m}$: angle between μ and m.
$g_{abs,cal}$: absorption dissymmetry factor calculated by $g_{abs,cal} = 4\cos\theta_{\mu,m} |\boldsymbol{\mu}||\boldsymbol{m}|/(|\boldsymbol{\mu}|^2+|\boldsymbol{m}|^2)$

The cartesian coordinates of all the optimized structures are listed as follows:

(*P*,*P*)-**1**

	X	Y	Z		X	Y	Z
S	0.8417733	-4.8929686	2.5196974	C	1.4650154	4.5135795	2.0303200
S	-0.8434957	-4.8930785	-2.5187795	C	0.7211453	3.4134803	1.4513887
S	0.8380943	4.9171362	-2.5158093	C	1.3989074	2.3276967	0.7729471
S	-0.8363678	4.9170796	2.5166424	C	0.6879693	1.2118940	0.1859098
N	-0.7092638	-5.4198762	2.6468308	C	1.3922208	0.0111662	0.0025123
N	0.5886015	-3.5097410	1.6740824	C	0.6891518	1.2328954	0.1841331
N	0.5864277	3.5325648	-1.6716192	C	0.6895665	1.2326550	0.1843759
N	-0.7138786	5.4421868	-2.6420123	C	1.3922218	0.0106919	0.0023089
N	-0.5898142	-3.5097185	-1.6735320	C	0.6875578	1.2121348	0.1856655
N	0.7073394	-5.4206305	-2.6457071	C	1.3981099	2.3282401	0.7725835
N	0.7158131	5.4414206	2.6431635	C	0.7199558	3.4139355	1.4507779
N	-0.5852151	3.5326100	1.6721347	C	1.4634173	4.5144793	2.0293852
C	-1.4682105	4.5343598	-2.0263628	C	2.8827024	4.5299337	1.9560440
C	-0.7229964	3.4345357	-1.4487484	H	3.4344360	5.3606444	2.3761538
C	-2.8877029	4.5477988	-1.9526127	C	3.5007873	3.4565721	1.3972879
H	-3.4404454	5.3787159	-2.3710057	H	4.5809465	3.4478207	1.3918526
C	-3.5045997	3.4731477	-1.3955668	C	2.7978882	2.3317929	0.8319787
H	-4.5846940	3.4638667	-1.3894709	C	3.5414764	1.1682439	0.3586246
C	-2.8004542	2.3473871	-0.8323877	C	2.8255223	0.0093279	0.0000135
C	-1.3996380	2.3466584	-0.7718290	C	3.5417778	1.1819555	0.3617958
C	-3.5413886	1.1830448	-0.3619726	C	4.9456422	1.1517902	0.3367323
C	-4.9452779	1.1530951	-0.3376078	H	5.4920441	2.0449073	0.5906917
H	-5.4914257	2.0462764	-0.5918816	C	5.6645083	0.0075425	0.0064159
C	-5.6645047	0.0089451	-0.0077456	C	4.9397069	1.1386468	0.3267213
C	-7.2041721	-0.0327201	-0.0001696	H	5.4911336	2.0319109	0.5785510

C	-7.8297329	1.3214090	-0.3820849	C	2.8012535	2.3463643	0.8326876
H	-7.5453268	2.1132776	0.3163096	C	1.4004372	2.3461196	0.7721888
H	-7.5466714	1.6323210	-1.3915430	C	0.7241871	3.4340910	1.4493454
H	-8.9194409	1.2397517	-0.3585914	C	1.4698167	4.5334487	2.0273229
C	-7.6945363	-1.0911059	-1.0156368	C	2.8893210	4.5463121	1.9537365
H	-7.3569596	-0.8482857	-2.0267520	H	3.4423668	5.3768173	2.3725459
H	-7.3277806	-2.0910731	-0.7728637	C	3.5058234	3.4716131	1.3963468
H	-8.7880132	-1.1308386	-1.0217595	H	4.5859150	3.4618083	1.3904578
C	-7.7038932	-0.4074725	1.4146038	C	7.2041666	0.0343398	0.0021067
H	-7.3744276	0.3281203	2.1532318	C	7.7029549	0.4091005	1.4172082
H	-8.7973033	-0.4415218	1.4323372	H	8.7963483	0.4433025	1.4356256
H	-7.3366895	-1.3862449	1.7318921	H	7.3354097	1.3878096	1.7342956
C	-4.9400661	-1.1373564	0.3258054	H	7.3731285	0.3265642	2.1556022
H	-5.4917447	-2.0305692	0.5772816	C	7.6950261	1.0928320	1.0130115
C	-3.5418637	-1.1671652	0.3584164	H	8.7885030	1.1326424	1.0185153
C	-2.8255211	0.0102283	-0.0000074	H	7.3580407	0.8500599	2.0243353
C	-2.7986876	-2.3307861	0.8322382	H	7.3280689	2.0927588	0.7703771
C	-3.5020063	-3.4550801	1.3979831	C	7.8301423	1.3196891	0.3794895
H	-4.5821645	-3.4458361	1.3926990	H	8.9198256	1.2378961	0.3552927
C	-2.8843117	-4.5284870	1.9570863	H	7.5453893	2.1116434	0.3186672
H	-3.4363462	-5.3588108	2.3775652	H	7.5477649	1.6305681	1.3891503
S	0.8417733	-4.8929686	2.5196974	C	1.4650154	4.5135795	2.0303200

(*M*,*M*)**-1**

	X	Y	Z		X	Y	Z
S	-0.8411389	-4.8931964	2.5195851	C	1.4655865	-4.5135305	2.0301245
S	0.8441626	-4.8932043	-2.5181206	C	0.7215739	-3.4134714	1.4513020
S	-0.8387471	4.9171553	-2.5154309	C	1.3991912	-2.3275594	0.7729213
S	0.8357114	4.9173176	2.5166645	C	0.6881081	-1.2117945	0.1859924
N	0.7099582	-5.4199536	2.6466028	C	1.3922253	0.0113400	0.0025865
N	-0.5881540	-3.5098914	1.6740423	C	0.6890215	1.2329973	-0.1840283
N	-0.5868846	3.5325928	-1.6712895	C	-0.6897034	1.2326114	0.1844602
N	0.7131616	5.4423754	-2.6417192	C	-1.3922248	0.0105703	-0.0022330
N	0.5902756	-3.5097781	-1.6730474	C	-0.6874281	-1.2121863	-0.1855434
N	-0.7066104	-5.4209054	-2.6451602	C	-1.3978411	-2.3283986	-0.7724108
N	-0.7165472	5.4414113	2.6432095	C	-0.7195251	-3.4140969	-1.4504330
N	0.5847543	3.5327714	1.6722259	C	-1.4628309	-4.5147767	-2.0289767
C	1.4676322	4.5345958	-2.0261682	C	-2.8821200	-4.5303687	-1.9557347
C	0.7225712	3.4346713	-1.4485543	H	-3.4337436	-5.3611832	-2.3757815
C	2.8871282	4.5481834	-1.9525020	C	-3.5003571	-3.4570151	-1.3971249
H	3.4397616	5.3791825	-2.3708736	H	-4.5805167	-3.4483914	-1.3917432
C	3.5041748	3.4735779	-1.3955291	C	-2.7976139	-2.3321028	-0.8318789
H	4.5842701	3.4644279	-1.3894730	C	-3.5413458	-1.1685933	-0.3586528
C	2.8001836	2.3477124	-0.8323582	C	-2.8255268	0.0090572	-0.0000167

C	1.3993715	2.3468381	-0.7717302	C	-3.5419193	1.1816245	0.3617125
C	3.5412595	1.1834339	-0.3620122	C	-4.9457808	1.1513389	0.3365222
C	4.9451564	1.1536158	-0.3377453	H	-5.4922824	2.0444172	0.5904027
H	5.4912033	2.0468483	-0.5920517	C	-5.6645128	0.0070251	0.0061480
C	5.6645108	0.0095296	-0.0079396	C	-4.9395832	-1.1391162	-0.3268747
C	7.2041899	-0.0320090	-0.0005091	H	-5.4909118	-2.0324376	-0.5787097
C	7.8296003	1.3220676	-0.3828676	C	-2.8015390	2.3461095	0.8326415
H	7.5450789	2.1141317	0.3152612	C	-1.4007188	2.3460199	0.7722113
H	7.5465136	1.6326036	-1.3924360	C	-0.7246252	3.4340874	1.4493749
H	8.9193197	1.2405437	-0.3593324	C	-1.4704144	4.5333462	2.0273392
C	7.6945190	-1.0906442	-1.0157347	C	-2.8899171	4.5460330	1.9537177
H	7.3568311	-0.8481211	-2.0268854	H	-3.4430817	5.3764542	2.3725344
H	7.3278339	-2.0905623	-0.7726379	C	-3.5062685	3.4712657	1.3962904
H	8.7879995	-1.1303161	-1.0219433	H	-4.5863587	3.4613215	1.3903722
C	7.7040962	-0.4063347	1.4143118	C	-7.2041731	-0.0349974	-0.0025059
H	7.3746276	0.3294179	2.1527813	C	-7.7028215	-0.4094221	-1.4177478
H	8.7975134	-0.4402602	1.4319387	H	-8.7962145	-0.4436459	-1.4362707
H	7.3370298	-1.3850659	1.7318901	H	-7.3352246	-1.3880466	-1.7350407
C	4.9402040	-1.1368525	0.3256203	H	-7.3729431	0.3264380	-2.1559260
H	5.4919834	-2.0300302	0.5769937	C	-7.6949956	-1.0938148	1.0122905
C	3.5420059	-1.1667932	0.3583297	H	-8.7884692	-1.1337818	1.0176626
C	2.8255269	0.0105446	-0.0000126	H	-7.3581512	-0.8512470	2.0237129
C	2.7989746	-2.3305071	0.8321422	H	-7.3278573	-2.0936241	0.7694346
C	3.5024388	-3.4547622	1.3977859	C	-7.8303036	1.3188726	0.3794076
H	4.5825946	-3.4454007	1.3924543	H	-8.9199796	1.2370200	0.3549758
C	2.8848823	-4.5282775	1.9568366	H	-7.5454511	2.1110646	-0.3184419
H	3.4370263	-5.3585748	2.3772225	H	-7.5481395	1.6294409	1.3892241

(*P*,*M*)**-1**

	X	Y	Z		X	Y	Z
C	0.707242	1.224546	-0.21584	C	1.665416	4.644416	1.764462
C	1.364481	-0.03534	-0.29517	C	0.865398	3.509022	1.349163
C	-0.64222	1.259738	0.216507	C	0.682761	-3.55088	-1.34576
C	-1.34466	2.449845	0.684339	C	1.423878	4.726121	1.759516
C	-2.82761	4.798388	1.542773	N	0.68721	-5.64052	2.388027
C	-3.44405	3.703902	1.023312	N	0.599492	3.599965	1.705484
C	-2.74016	2.509278	0.632695	N	0.412537	3.622492	1.709937
C	-3.48808	1.310937	0.276489	N	0.976501	-5.59363	2.39567
C	-4.85892	1.321088	-0.02058	N	-0.6872	5.640547	2.387927
C	-5.58586	0.147229	-0.21177	N	0.599502	3.599985	1.705402
C	-4.91673	-1.06661	-0.02211	N	0.976484	5.593664	2.395548
C	-3.55241	-1.13111	0.273787	S	0.836417	5.031753	2.470956
C	-2.8663	-2.36662	0.631818	S	0.575705	5.062623	2.478836
C	-3.63025	-3.52282	1.023953	S	0.83643	5.031788	2.470845

C	-3.0706	-4.64628	1.546182	N	0.412549	3.622511	1.709842
C	1.470262	2.37749	-0.68453	S	0.575725	5.062662	2.478705
C	2.802667	-0.07287	-0.3266	H	3.373613	5.682962	1.843477
C	-7.07823	0.144453	-0.59035	H	4.521304	3.717438	0.929702
C	-7.64483	1.566639	-0.75453	H	5.359903	2.271168	0.124776
C	-7.26412	-0.60415	-1.93098	H	5.472866	1.987995	0.126447
C	-7.88937	-0.57166	0.514803	H	4.706785	3.482215	0.929183
C	-0.70724	-1.22456	0.215849	H	3.660959	5.501521	1.847898
				H	8.699131	1.509132	-
C	-1.36448	0.035326	0.295169				1.037111
C	0.642218	-1.25976	-0.21651	H	7.124541	2.124761	1.537626
C	1.34466	-2.44986	-0.68436	H	7.585701	2.139109	0.175247
				H	-	0.616188	2.213558
C	2.827605	-4.79839	-1.54283		8.321117		
C	3.444044	-3.70391	-1.02334	H	6.924309	1.640433	1.869819
C	2.740156	-2.50929	-0.63272	H	6.703251	0.115876	2.732284
C	3.488078	-1.31095	-0.2765	H	-7.76839	0.067134	1.477165
C	4.858923	-1.32111	0.020562	H	7.577231	1.610905	0.641133
C	5.585867	-0.14725	0.211754	H	-8.95395	0.573429	0.262411
C	4.916732	1.066592	0.022113	H	3.373614	5.682958	1.843538
C	3.552412	1.131091	-0.27378	H	4.521302	3.717452	0.929725
C	2.8663	2.366613	-0.63179	H	5.359905	2.271188	0.124748
C	3.630245	3.522821	-1.02391	H	5.47287	1.987974	0.126452
C	3.070597	4.646286	-1.54611	H	4.706784	3.482211	0.929149
C	-1.47026	-2.3775	0.684563	H	3.66095	5.501536	1.847812
C	-2.80267	0.072849	0.326604	H	8.699137	-1.50916	1.037077
C	7.078235	-0.14448	0.590329	H	7.12455	2.124784	1.537607
C	7.644833	-1.56667	0.754505	H	7.585694	2.139137	0.175269
C	7.26413	0.604124	1.930957	H	8.321134	0.616161	2.213528
C	7.88937	0.571632	-0.51483	H	6.924326	1.640409	1.869798
C	-0.68276	3.550886	1.345703	H	6.70327	0.115852	2.732264
C	-1.42388	4.726132	1.759446	H	7.768385	0.067106	1.477191
C	0.865392	3.50903	-1.34909	H	7.577232	1.610878	-0.64116
C	1.665406	4.644433	-1.76437	H	8.953952	0.5734	0.262445

TS

	X	Y	Z		X	Y	Z
C	3.294802	1.588842	-0.80406	C	4.324967	-2.506	-0.79066
C	4.16502	2.574542	-1.40461	H	4.593578	-3.54956	-0.75661
C	2.25478	1.979916	0.048848	C	5.201652	-1.60723	-1.38827
C	1.107172	1.075082	0.231412	C	4.798102	-0.27204	-1.46427
C	1.379474	-0.33236	0.080205	H	5.481145	0.450744	-1.88659
C	0.37645	-1.3347	0.301484	C	6.571498	-2.02586	-1.95261
C	0.740228	-2.74085	0.156829	C	7.688893	-1.26396	-1.20194

C	2.48636	-4.48966	0.284263	H	8.670023	-1.55212	-1.59123
C	2.087425	-3.11487	0.093712	H	7.591767	-0.18176	-1.31459
C	-1.84655	2.934993	-1.01125	H	7.66655	-1.49148	-0.13285
C	-2.17724	4.235078	-1.55054	C	6.833468	-3.53495	-1.79625
C	-0.845	2.814926	-0.03583	H	6.835462	-3.84167	-0.74675
C	-0.2709	1.474529	0.210352	H	6.092373	-4.13575	-2.33055
C	-1.24489	0.446553	0.169223	H	7.814676	-3.77941	-2.21107
C	-0.94276	-0.88662	0.54431	C	6.635213	-1.6801	-3.45833
C	-2.06909	-1.6266	1.100383	H	6.506297	-0.6101	-3.63612
C	-4.49607	-2.03872	1.230374	H	7.605147	-1.97149	-3.87228
C	-3.3677	-1.34885	0.671649	H	5.855511	-2.208	-4.01393
H	4.774678	2.264616	-2.24299	C	2.5332	3.228191	0.73209
H	3.537491	-4.69669	0.432953	N	2.137989	3.534902	1.960471
H	-2.78005	4.27349	-2.44866	C	3.515454	4.168505	0.211535
H	-5.48181	-1.79085	0.856796	S	2.888127	4.934335	2.383694
C	-2.71093	1.787984	-1.27288	N	3.768873	5.193091	1.016428
C	-2.53433	0.665986	-0.43173	C	-3.08543	-3.21353	2.756071
C	-3.54958	-0.31275	-0.33874	C	-1.92585	-2.5518	2.192525
C	-4.66104	-0.2151	-1.17801	N	-0.78935	-2.87049	2.81122
H	-5.42127	-0.98387	-1.1284	N	-2.79969	-4.02138	3.777348
C	-3.82168	1.819647	-2.12894	S	-1.1754	-3.93195	4.002332
C	-4.79736	0.820839	-2.1119	C	-0.18987	-3.83469	-0.0653
C	-6.0121	0.834809	-3.059	C	0.244214	-5.21736	0.035076
C	-6.0045	-0.45221	-3.91697	N	-0.7032	-6.10926	-0.23634
H	-6.06392	-1.35276	-3.30177	N	-1.45144	-3.73072	-0.47316
H	-6.86033	-0.45711	-4.5987	S	-2.04419	-5.25249	-0.64964
H	-5.09209	-0.51665	-4.51577	C	-1.18352	5.290936	0.319544
C	-7.31562	0.891511	-2.22872	C	-0.72226	3.99492	0.791352
H	-7.34807	1.794491	-1.61317	N	-1.16401	6.244413	1.244642
H	-8.18624	0.899886	-2.8913	N	-0.45475	3.987634	2.092977
H	-7.4137	0.03018	-1.56402	S	-0.69329	5.515131	2.646294
C	-6.00039	2.043244	-4.01294	C	1.606653	-5.52148	0.314065
H	-6.04636	2.991929	-3.47109	C	-4.38334	-2.95291	2.234329
H	-5.11153	2.051047	-4.64978	C	-1.79594	5.398843	-0.96412
H	-6.87349	1.998946	-4.66901	C	4.234902	3.85997	-0.97852
H	-3.93688	2.653864	-2.80392	H	4.881049	4.596502	-1.43736
C	3.576303	0.173211	-0.9505	H	-2.05884	6.368306	-1.36621
C	2.678953	-0.7583	-0.36555	H	1.912521	-6.54651	0.476603
C	3.066195	-2.11855	-0.29911	H	-5.24313	-3.45198	2.661806

5. Circular Dichroism in Thin Film

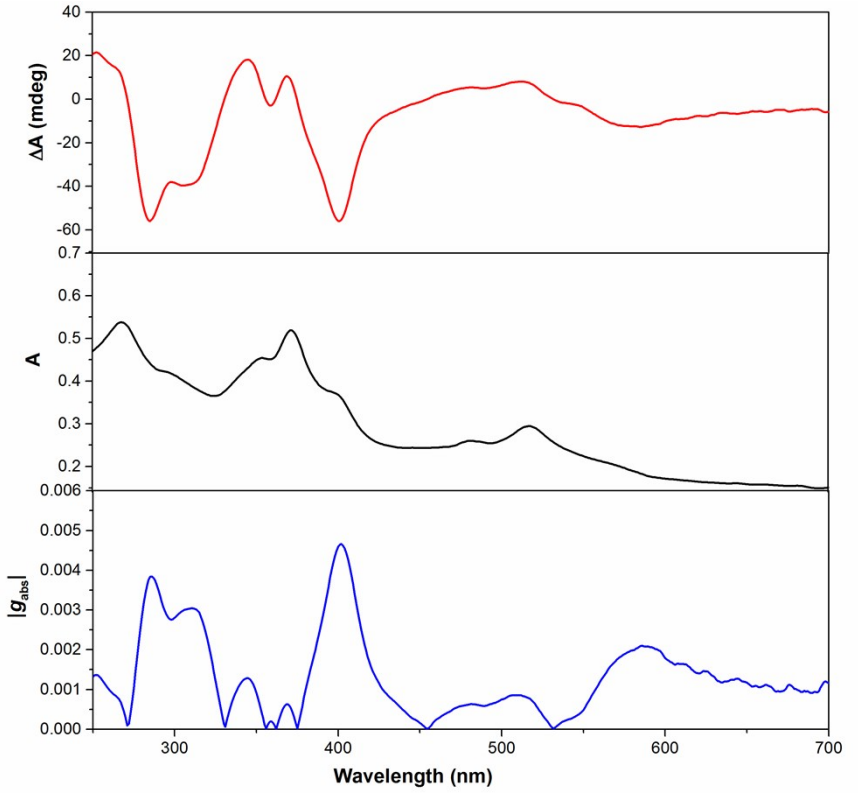


Figure S13. Circular dichroism (top) and absorption (middle) spectra as well as the absolute absorption dissymmetry factor ($|g_{abs}|$) curve (bottom) of the drop-casted thin film of (*M*,*M*)-**1**. The absorption dissymmetry factor was calculated by $g_{abs} = \Delta A/A^3$, where ΔA (mdeg) is converted to ΔA (a.u.) by ΔA (a.u.) = ΔA (mdeg) / 32982.

6. NMR and HRMS Spectra

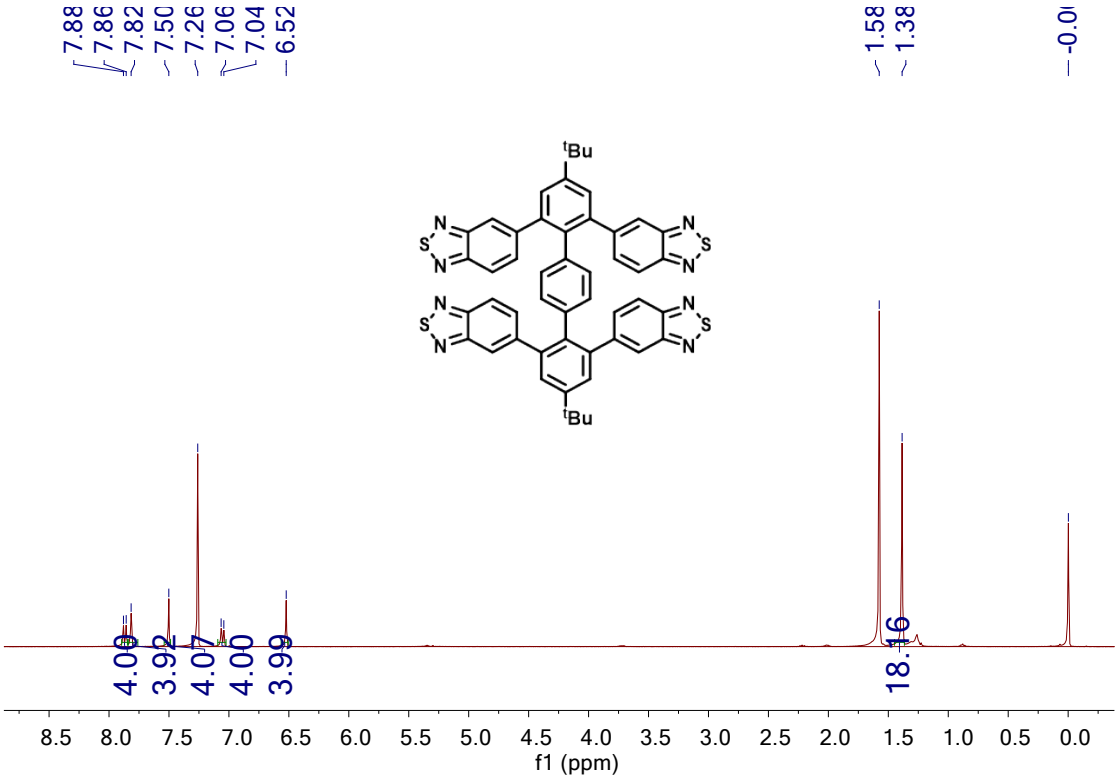


Figure S14. ^{1}H NMR spectrum of **TBTP** (400 MHz, $CDCl_3$).

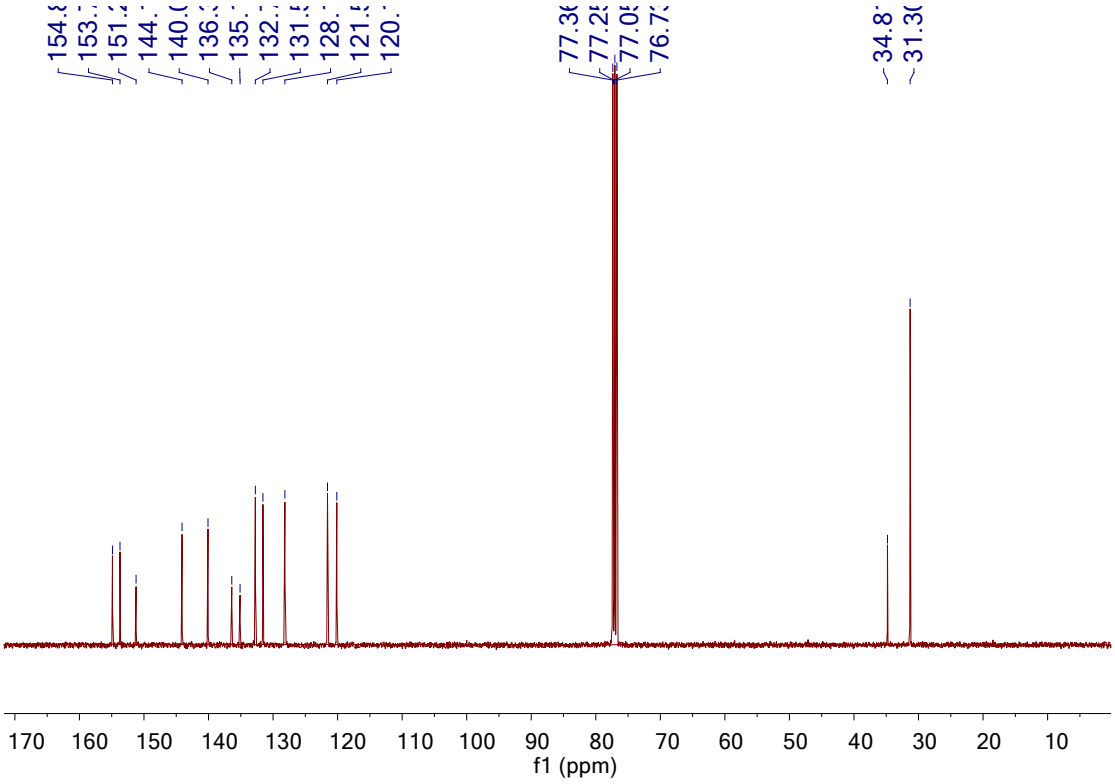


Figure S15. ^{13}C NMR spectrum of **TBTP** (100 MHz, $CDCl_3$).

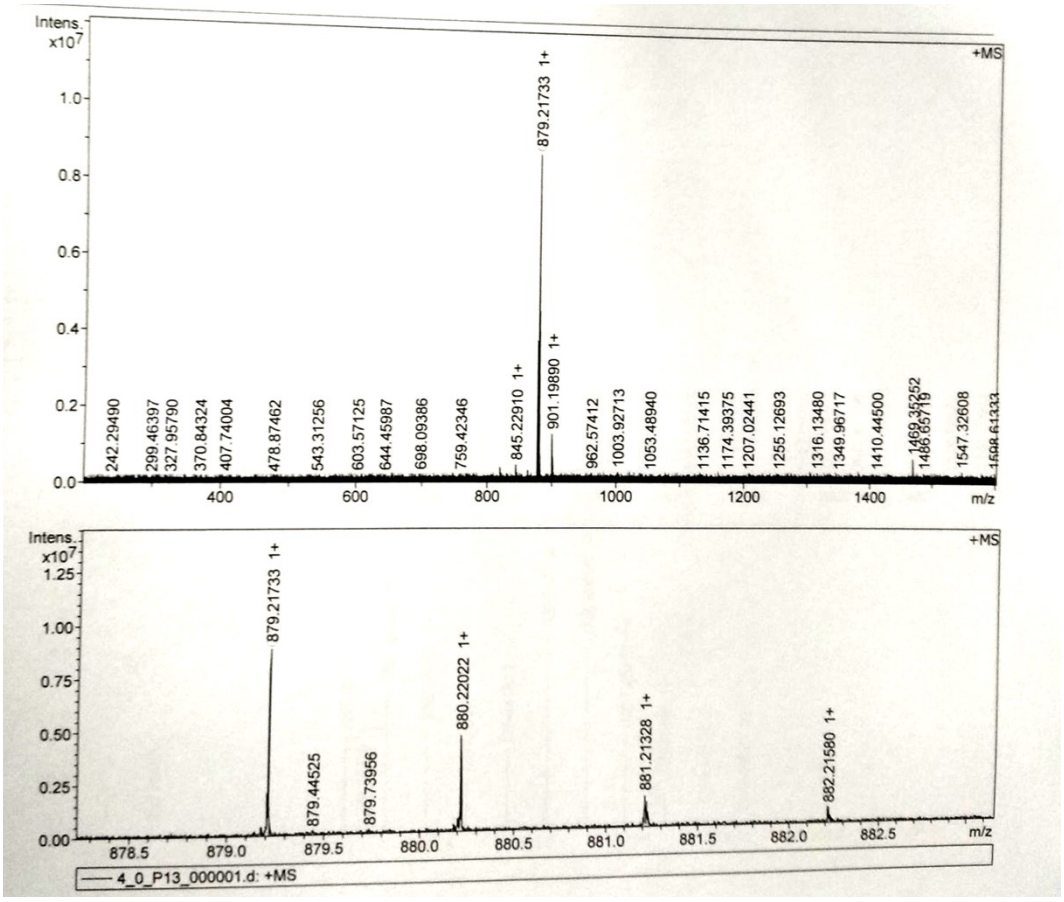


Figure S16. HRMS (MALDI-TOF) spectrum of **TBTP**.

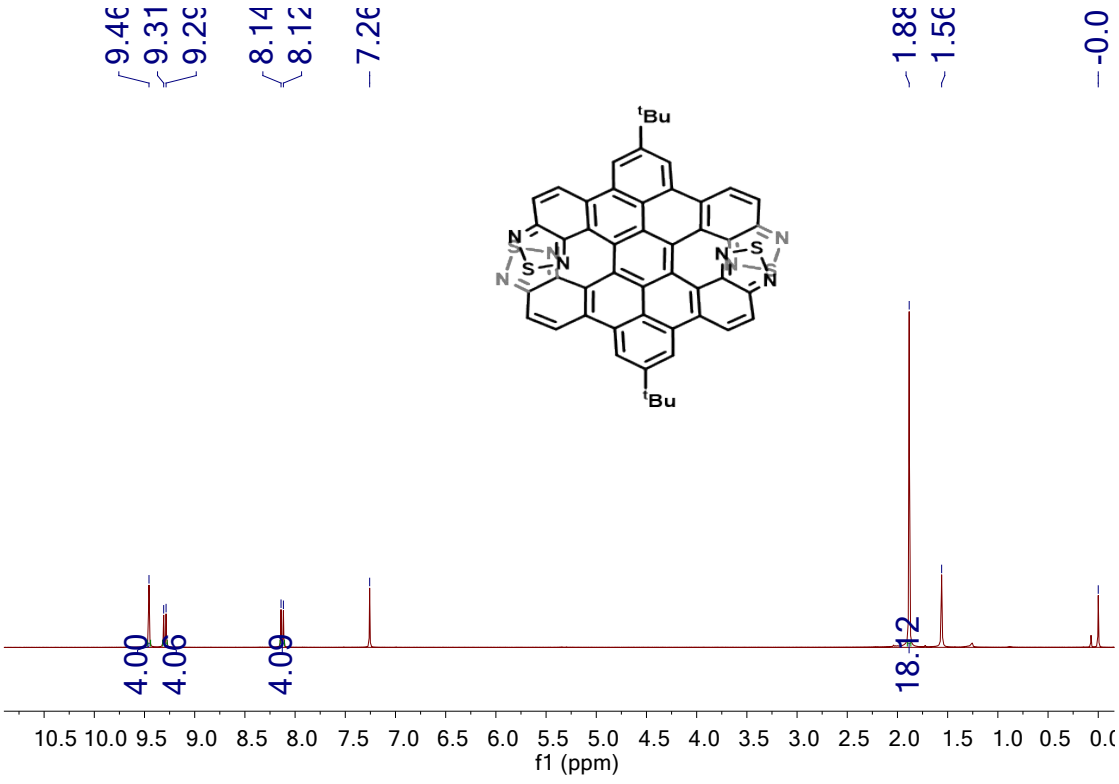


Figure S17. ^{1}H NMR spectrum of **1** (400 MHz, $CDCl_3$).

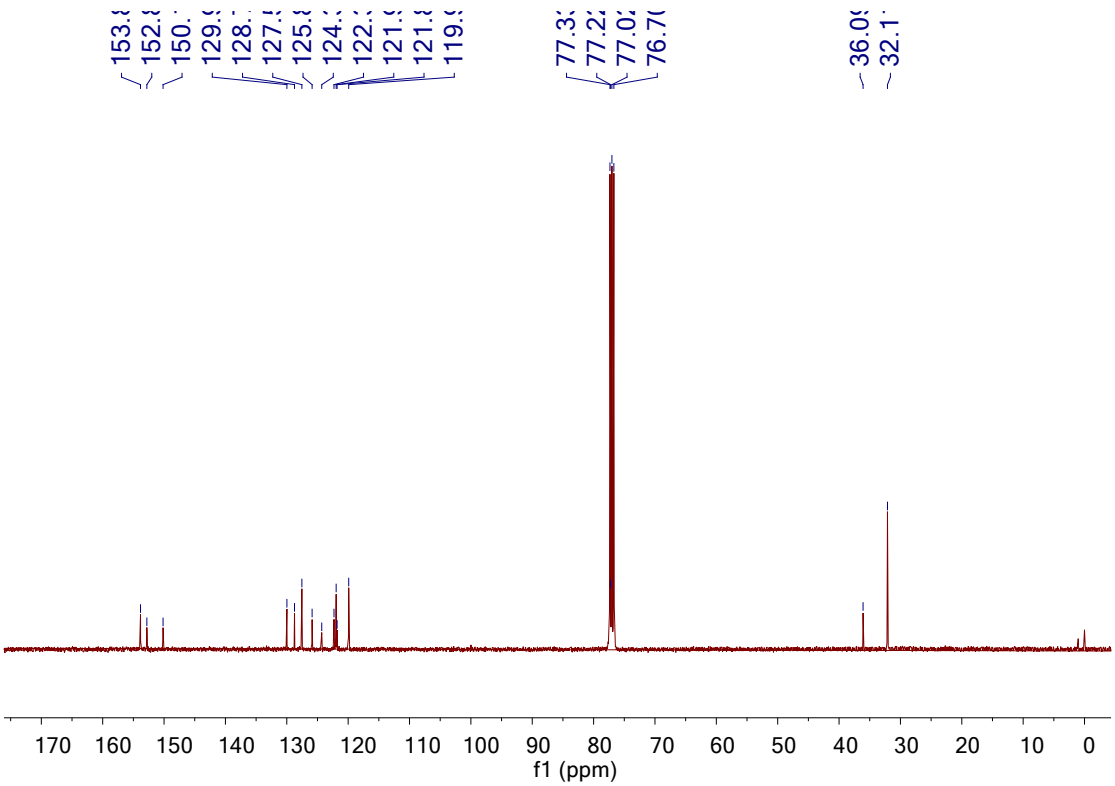


Figure S18. ^{13}C NMR spectrum of **1** (100 MHz, $CDCl_3$).

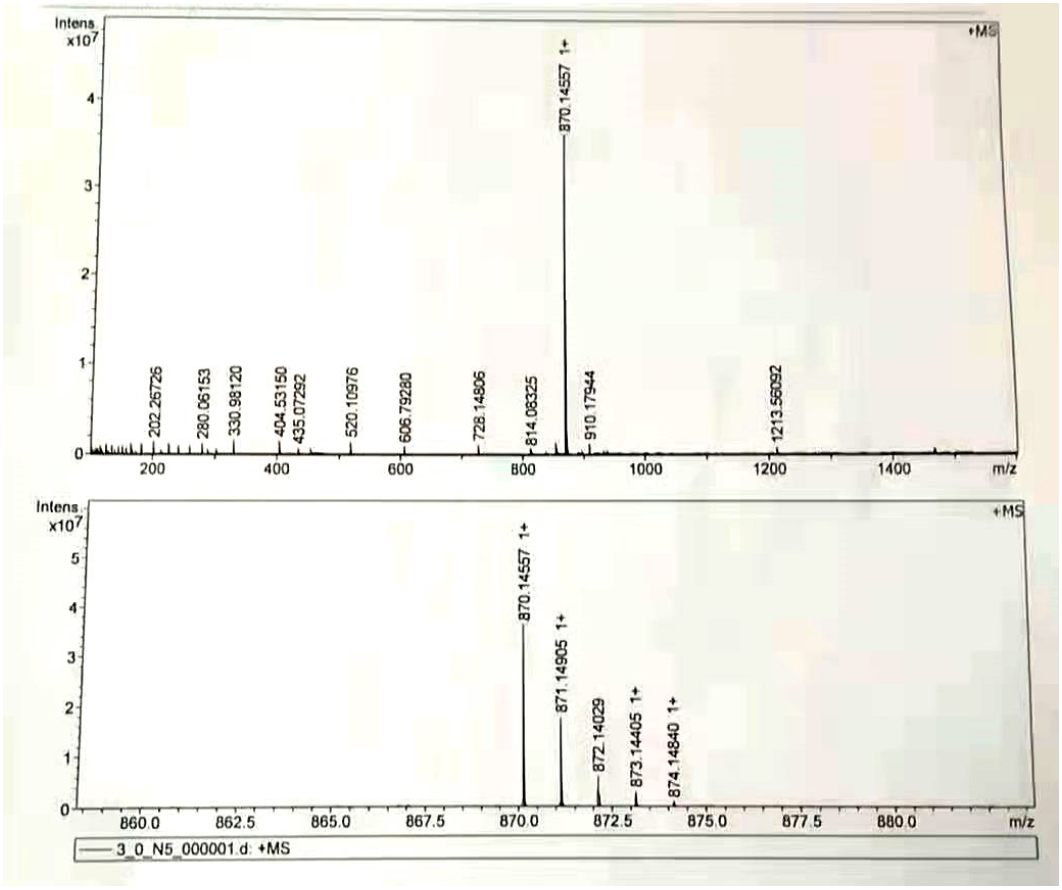


Figure S19. HRMS (MALDI-TOF) spectrum of **1**.

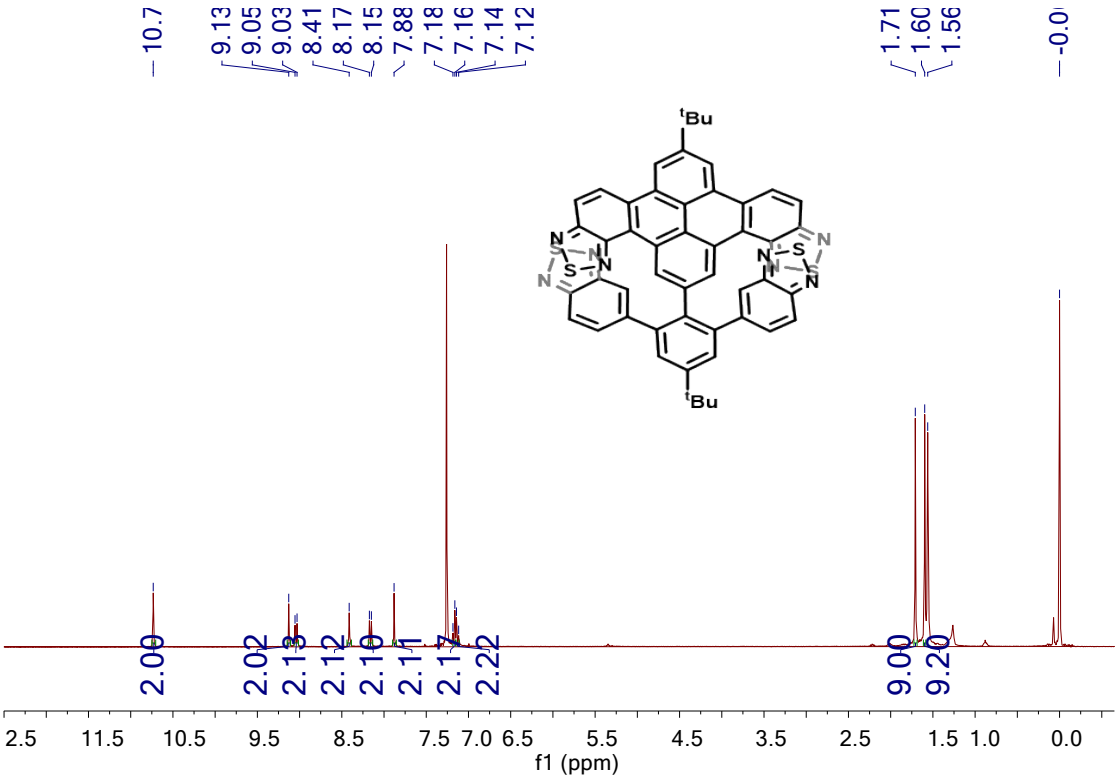


Figure S20. ^{1}H NMR spectrum of **2** (400 MHz, $CDCl_3$).

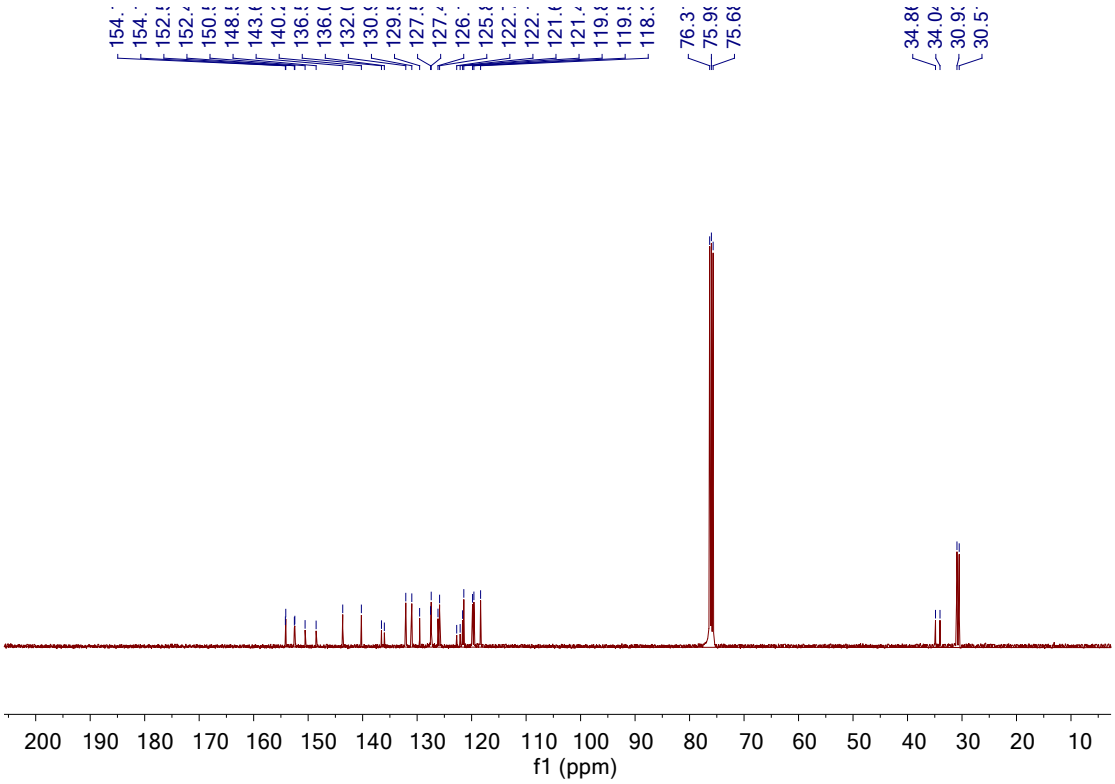


Figure S21. ^{13}C NMR spectrum of **2** (100 MHz, $CDCl_3$).

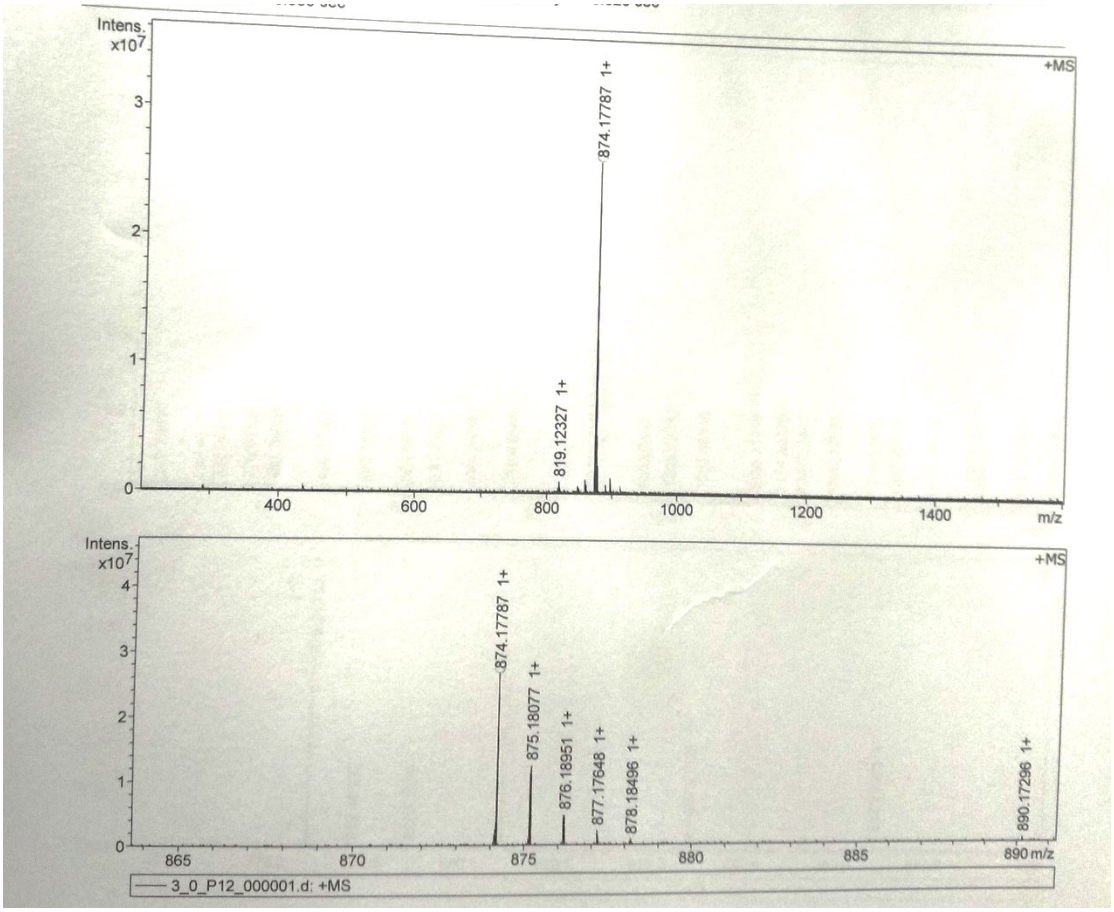


Figure S22. HRMS (MALDI-TOF) spectrum of **2**.

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